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DEVELOPMENT OF AN IMPROVED OXYGEN ELECTRODE FOR USE
IN ALKALINE H₂-O₂ FUEL CELLS

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DEVELOPMENT OF AN IMPROVED OXYGEN ELECTRODE FOR USE
IN ALKALINE H_2-O_2 FUEL CELLS

The objective of this project is the synthesis of interstitial compounds for increasing the efficiency of the oxygen electrode in alkaline H_2-O_2 fuel cells. The work is being carried out for the National Aeronautics and Space Administration with Mr. E. M. Cohn as technical monitor. Principal investigators are D. Bienstock, R.C. Diehl, and C.T. Grein.

Bureau of Mines
Pittsburgh Coal Research Center

Quarterly Report for the period ending September 30, 1966

Development of An Improved Oxygen Electrode for Use
in Alkaline H₂-O₂ Fuel Cells

Summary

An apparatus was built for preparing catalysts for use as the oxygen electrode in the alkaline H₂-O₂ fuel cell. It consists of four units which can be operated independently to reduce, carbide, or nitride 50 to 100 cc batches of catalyst preparations.

Twenty-four samples have been submitted to Tyco Laboratories for fuel-cell testing. These include epsilon, chi, and theta iron carbides, gamma, epsilon, and zeta iron nitrides, iron carbonitrides, and iron nitrocarbides prepared from leached Raney iron and from a reduced alkali-promoted magnetite.

An induction furnace has been modified to accommodate preparations of 1-pound batches of Raney alloys under an inert atmosphere or under vacuum.

Introduction

The objective of this project is the development of catalysts to improve the efficiency of the oxygen electrode in alkaline H₂-O₂ fuel cells.

Tyco Laboratories, Waltham, Mass., has shown that an interstitial compound, Hägg carbide (Fe₂C), has a high activity for O₂ reduction. Although its activity is lower than platinum, palladium, silver, and gold it is considerably better than iron. The partial success of this interstitial compound has opened up a large group of potential catalysts. It is these catalysts that this project is engaged upon preparing.

A careful and intensive literature search has been conducted on carbides, nitrides, carbonitrides, nitrocarbides, and borides of iron, cobalt and nickel. Basic research on carbides was done by Hägg in the 1930's (1). He used the procedure of Bahr and Jessen (2-4) and prepared carburized products at several temperatures.

The carbides of iron, nickel and cobalt were first prepared by the Federal Bureau of Mines in the early forties in its study of the Fischer-Tropsch synthesis. In 1944, Hofer (5) published a report on the preparation and properties of metal carbides. From 1946-63 the Bureau turned out considerable amount of work in regard to metal carbides, nitrides, and carbonitrides (6,7).

In 1960 Johnston, Heikes and Petrolo (8,9) of the Westinghouse Research Laboratories in Pittsburgh used leached Raney iron, rather than a reduced magnetite promoted with K_2O preferred by the Bureau, in the preparation of the carbide. Because of the ease in preparation and higher purity of the carbide obtained, this technique will be examined more closely by us.

Experimental Procedure

Apparatus

Apparatus was constructed to allow flexibility and productivity in preparing interstitial compounds by gas-phase reactions. The equipment is shown in figure 1. Four separate units can be operated independently of each other. To each unit a manifold of 6 gases, H_2 , N_2 , CO_2 , CO , H_2+CO , and NH_3 , is connected. Each unit is provided with an electrically heated reactor and gas-preheat zone. The preparation being made is held in the horizontal Vycor tube as a fixed bed approximately 5 inches in length and 1 inch in diameter and confined by stainless steel screens. Three thermocouples are located axially in the front, middle, and end of bed and are continuously recorded. One of the 3 thermocouples may act as the sensing element for the temperature controller. The controller is a Pyrovane unit automatically operating a high and low level of electrical heating of the reactor. The preheat zone is a cylindrical form-fitting cage of 1/4" glass beads which can be readily removed during discharge of catalyst. The carbiding operation is a highly exothermic reaction and if not closely controlled would result in hot spots, runaway temperatures, and deposition of free carbon. To monitor the carbide reaction 2 automatic systems are employed. When carbiding with a H_2+CO mixture, the gas effluent is monitored by a Lira infrared absorption unit. When reaction increases to the extent that 20% of the CO is consumed, all heats both high and low level are shut off. The heats are returned when the CO content returns to greater than 80% of the initial level. When carbiding with pure CO , a thermal conductivity unit is similarly employed. Thus at the start of the carbiding operation, the operator may set his temperature control to $350^\circ C$ and the CO monitor to

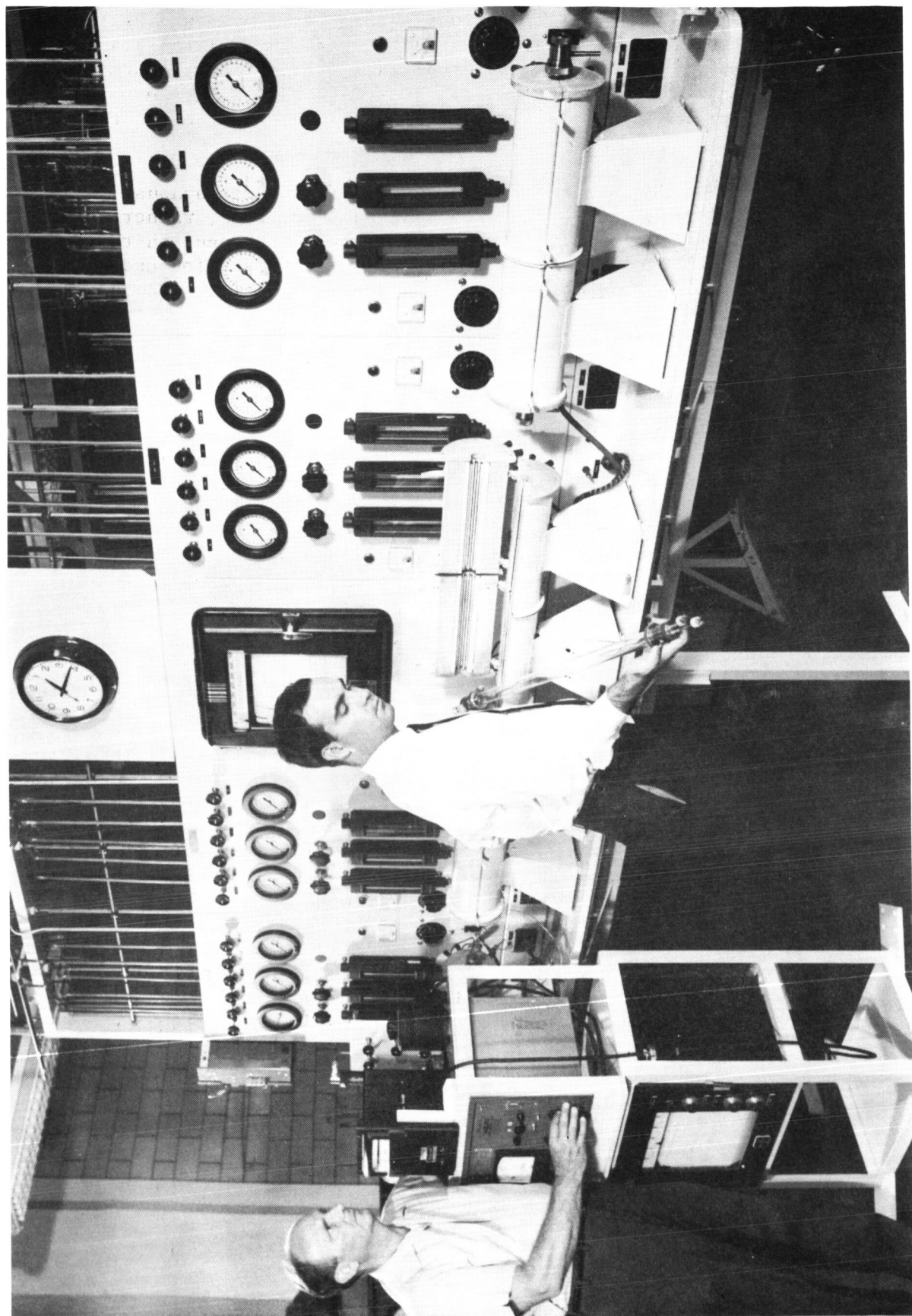


FIGURE 1. - Unit for Preparing Electrode Catalysts.

20% of CO consumed. Although reaction may start as low as 150°C, the bed temperature will gradually and consistently rise to 350°C, perhaps over a period of 24 hours, with the degree of reaction held to a maximum of 20% CO conversion. Both the temperature and CO content of the effluent are continuously recorded. With this type of control unattended overnight operations are possible. The infrared detection system is shown in figure 2.

Preparation of catalysts

The preparation of the catalysts is discussed under the following topics:

1. Raney iron preparations
2. Reduction of magnetite
3. Coprecipitated catalyst preparations
4. Carbide preparations
5. Nitride preparations
6. Nitrocarbide preparations
7. Carbonitride preparations

1. Raney iron preparations

Procedure

The procedure involves the leaching of aluminum in Raney iron (FeAl_2) with an excess of sodium hydroxide at a temperature not to exceed 80°C under an argon atmosphere. The remaining fine iron is washed with boiled distilled water ten times, pyridine five times, and then stored under pyridine for later use. Table 1 shows the experimental conditions employed in the earlier preparations. At present Raney iron, 150-200 mesh, in batches of 200 grams are used.

At the start of the ninth run the Raney iron was treated twice with fresh sodium hydroxide to increase the efficiency of leaching.



FIGURE 2. - Infrared Detection Apparatus for CO Monitoring.

TABLE 1.- Preparation of finely-divided iron by alkali leaching of Raney iron

Run no.	Quantity of Raney iron, g	Raney iron mesh size	Quantity of NaOH, g	Number of leachings	Total leaching time, hrs	Product recovered, percent		
						Fe	Al	Na
1-RI	90.00	170-200	242	1	2½	88.2	1.79	0.04
2-RI	do	do	do	1	2½	89.2	1.80	.04
3-RI	do	do	do	1	3	85.5	1.92	.04
4-RI	do	do	do	1	2	86.5	1.26	.04
5-RI	do	do	do	1	2	89.1	1.67	.04
6-RI	do	do	do	1	2	89.6	1.31	.03
7-RI	do	150-170	do	1	2	87.0	1.37	.02
8-RI	do	do	do	1	2	74.6	1.99	--
9-RI	do	do	906	2	3	93.5	0.70	.04
10-RI	do	200-250	600	2	3	89.1	1.73	.02
11-RI	do	do	do	2	3	91.2	1.52	.03
12-RI	do	do	do	2	3	92.0	1.20	.03
13-RI	do	170-200	do	2	2½	85.6	1.10	.03
14-RI	do	do	do	2	3	89.6	0.90	.03
15-RI	do	do	do	2	4			
4-RI ^{a/}	do	do	do	2	2	89.7	0.72	.03

a/ Retreatment.

Results

X-ray analysis of the leached Raney iron showed α -Fe as the major phase and Fe_3O_4 as the minor phase. The presence of Fe_3O_4 as a contaminant in the early preparations of carbide prepared from Raney iron could now be explained. By reducing the leached Raney iron with hydrogen at 450°C , elimination of Fe_3O_4 in later preparations of the iron carbides was achieved.

2. Reduction of magnetite

Procedure

An alkali-promoted magnetite, whose analysis is given below, was reduced with hydrogen at an hourly space velocity of 2,500 at 450°C for about 40-44 hours. The degree of reduction was determined by the amount of H_2O collected in a series of drying tubes, as shown in table 2 and figure 3.

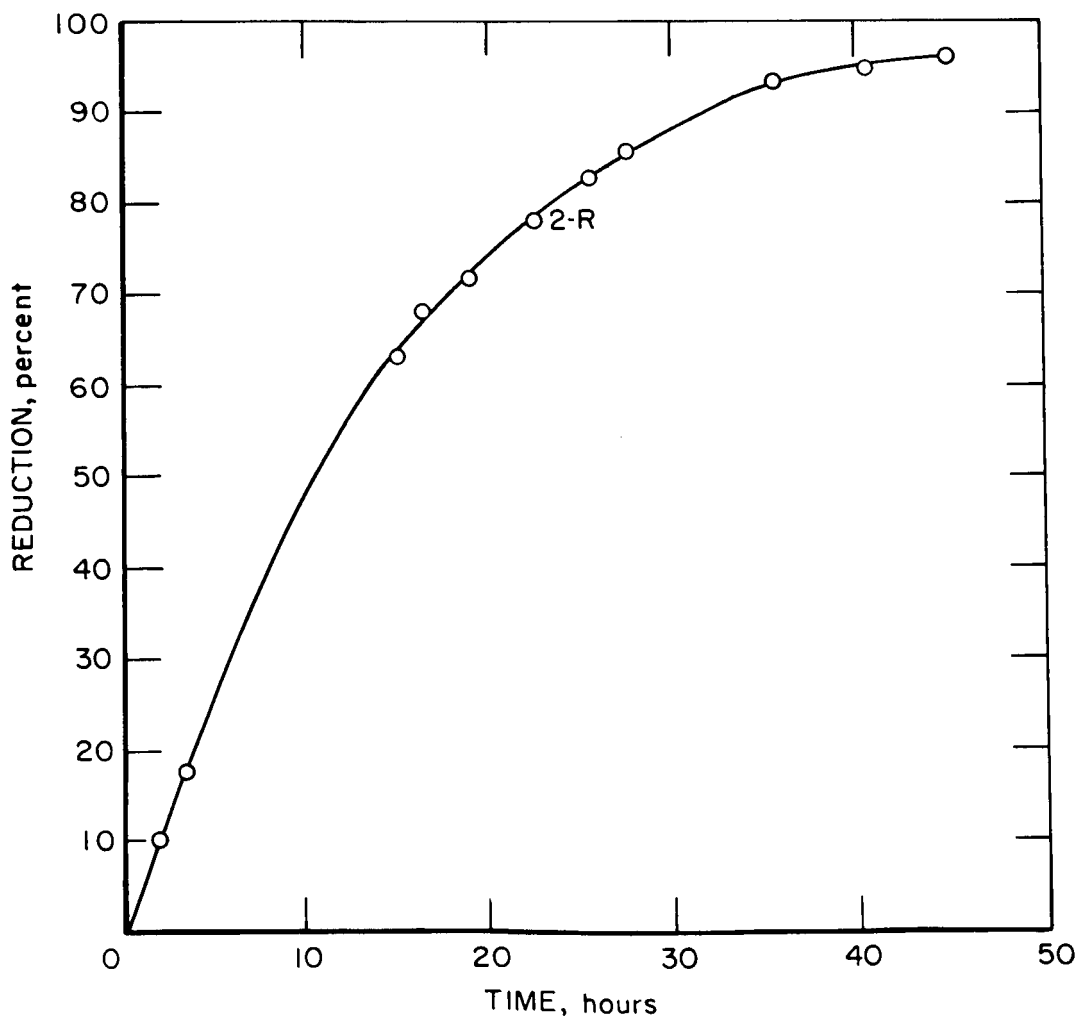


FIGURE 3. - Reduction of Alkali-Promoted Magnetite With H_2 at 450°C and an Hourly Space Velocity of 2,500.

TABLE 2.- Reduction of magnetite

Run no	Magnetite charged, g	Recoverable H ₂ O for 100% reduction, g ^{a/}	H ₂ O collected, g	Reduction, percent	Hourly space velocity, hr ⁻¹	Reaction time, hrs
1R	61.37	17.99	13.16	73.2 ^{b/}	10,000	10
			15.52	86.3	2,500	23
2R	64.72	18.97	18.18	95.8	2,500	44
3R	62.45	18.31	17.34	94.7	2,500	37
4R	61.44	18.01	17.19	95.5	2,500	44
5R	65.55	19.22	18.14	94.4	2,500	40
6R	62.43	18.30	16.75	91.5	2,500	43
7R	62.74	18.39	16.87	91.7	2,500	44
10R	67.32	19.73	18.69	94.7	2,500	33

a/ (Charge of magnetite)(0.2606)($\frac{18}{16}$) = weight of recoverable water.

b/ Low value because of failure to displace air in absorbent bottles with hydrogen.

Alkali-promoted magnetite

Fe ₃ O ₄ -----	93.46%
MgO -----	4.61
K ₂ O -----	0.57
SiO ₂ -----	0.71
Cr ₂ O ₃ -----	0.65
	<u>100.00</u>

Total iron = 67.40%

100% - (Total iron + MgO + K₂O + SiO₂ + Cr₂O₃) = Removable oxygen.

3. Coprecipitated catalyst preparations

This work was done to supplement our future alloying studies. In examining the phase diagram data (10) on the Fe-Ag and Co-Ag systems it is seen that the metals in both cases are not appreciably mutually soluble. It was thought that it would be more practical to prepare a mixture of oxides by coprecipitation, followed by reduction, nitriding, and carbiding.

Iron oxide-silver oxide mixtures were prepared by treating a mixed solution of iron and silver nitrates with Na₂CO₃. The precipitates were filtered, washed, and dried as shown in table 3. The mixed oxides were reduced and nitrided. A stock of iron-silver and cobalt-silver mixtures will be made and will be used to prepare interstitial compounds.

4. Carbide preparations

As carbiding plays a major role in this project, techniques of carbiding iron are discussed in detail in the Appendix. Nitriding and boriding are also covered.

TABLE 3.- Coprecipitation and reduction of mixed oxides of iron and silver

Run no	Reactants other than H ₂ O, g				Fe/Ag weight ratio of product	Reduction				
	Fe(NO ₃) ₃ ·9H ₂ O	AgNO ₃	Na ₂ CO ₃	Washings		Charge, g	Gas	Hourly space velocity, hr ⁻¹	Average of bed temp, °C	Duration of reduction, hrs
I-CP	46.62	3.38	150	H ₂ O, acetone, ethanol, and ether	3.04/1	55.35	H ₂	2,500	450	18
II-CP	41.07	8.93	150	H ₂ O, acetone, ethanol, and ether	1/1	71.12	H ₂	2,500	453	7
III-CP	30.25	19.75	150	H ₂ O, acetone, ethanol, and ether	1/3.0	66.25	H ₂	2,500	450	3.3

a. Procedure

A known weight of finely-divided iron under pyridine was transferred to a Vycor tube (figure 4). The pyridine was decanted under a strong stream of argon. The remaining pyridine was driven off under a flow of nitrogen at 110°-120°C for a period of 4-5 hours and recovered in a series of dry ice-trichloroethylene traps. The temperature was raised to 180°C and the nitrogen replaced with a flow of $10\text{H}_2+1\text{CO}$ gas at an hourly space velocity of 3,000. The maximum temperature was set and the bed temperature automatically and slowly raised to the desired level (see table 4) and remained at that level for the entire reaction time.

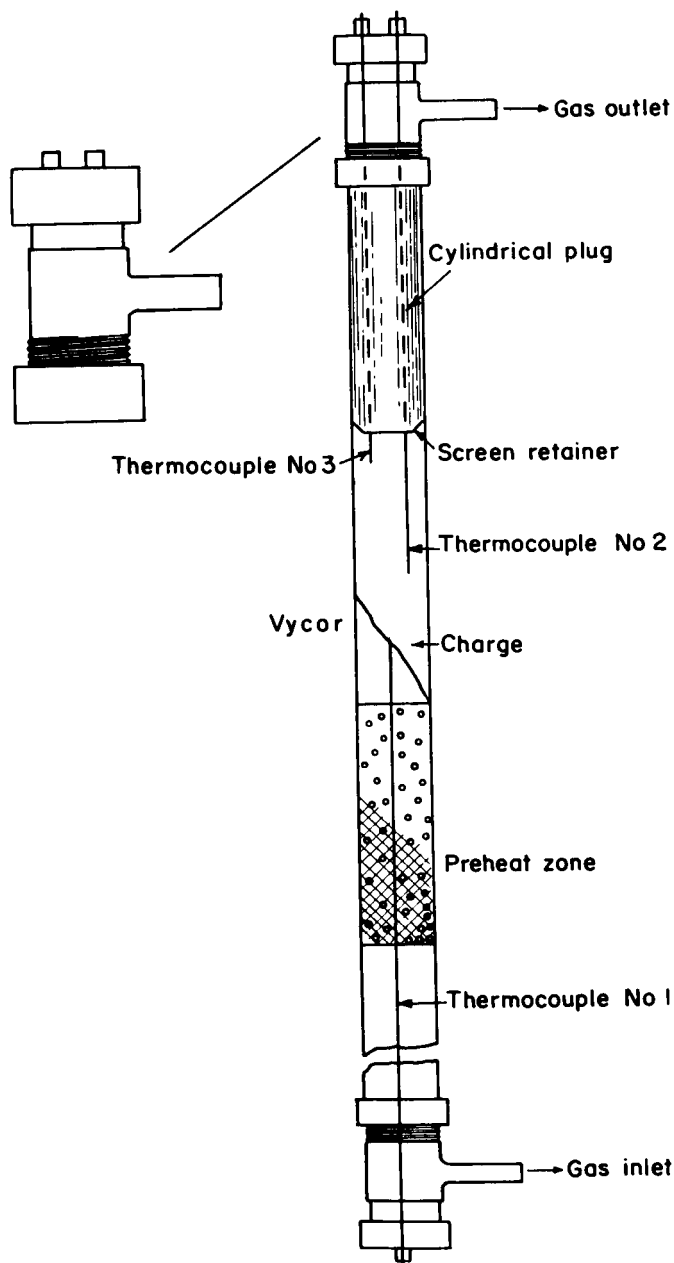


FIGURE 4. - Vycor Reaction Vessel.

TABLE 4.- Pretreatment and carburizing

Run no	Charge	Pretreatment				Carburization						Qualitative x-ray diffraction	Chemical analysis, wt-%		
		Charge wt	% Fe in charge	Hourly space velocity, hr ⁻¹	Reaction temp, °C	Reaction time, hrs	Gas	Hourly space velocity, hr ⁻¹	Temperature, °C				Discharge weight, g	Total Fe	Free C
									Start of bed	Middle of bed	Rear of bed				
1C	Leached Raney iron	43.44	93.50	--	--	--	10H ₂ +100	3000	190-212 (177)g/	--	190-240 (231)g/	Fe ₃ O ₄ , e-Fe ₂ C, x-Fe ₂ C, α-Fe	----	cancelled	----
2C	do	46.78	92.01	--	--	--	do	do	164-210 (210)	--	164-241 (215)	e-Fe ₂ C, Fe ₃ O ₄	78.50	6.60	3.60
3C	do	46.62	91.20	--	--	--	do	do	190-270 (262)	190-320 (304)	190-290 (277)	x-Fe ₂ C, Fe ₃ O ₄	77.80	4.90	3.45
4C	1C	--	--	--	--	--	do	do	167-220 (216)	167-288 (265)	165-250 (246)	x-Fe ₂ C, Fe ₃ O ₄	84.37	7.50	3.34
5C	b/	--	--	H ₂	450	10	do	do	--	252-253 (252)	233-238 (228)	x-Fe ₂ C, α-Fe	80.21	5.30	3.12
6C	Leached Raney iron	45.28	85.62	do	460	10	do	do	163-212 (195)	188-240 (230)	170-245 (230)	x-Fe ₂ C, θ-Fe ₃ C	--	--	--
7C	do	45.78	89.10	do	460	22	do	do	282-330 (322)	316-365 (361)	324-400 (385)	--	--	--	--
8C	Magnetite	131.32	67.40	do	460	41	CO	100	143-300 (152)	158-322 (226)	154-304 (209)	--	--	--	--
9C	do	131.30	--	do	460	49	CO	100	474-487 (481)	502-510 (505)	496-502 (498)	θ-Fe ₃ C, e-Fe ₂ C	81.57	9.25	4.39
10C	do	63.35	--	do	460	48	CO	100	150-180 (172)	169-199 (190)	143-182 (167)	x-Fe ₂ C	--	--	--
11C	do	128.50	--	do	450	44	CO	100	180-260 (235)	199-288 (261)	182-258 (236)	--	--	--	--
12C	Leached Raney iron	107.68	--	do	458	10	10H ₂ +100	3000	260-309 (290)	288-349 (322)	258-305 (287)	θ-Fe ₃ C, α-Fe	--	--	--
	do	--	--	do	450	44	CO	100	174-260 (235)	174-260 (235)	137-206 (183)	x-Fe ₂ C	17.31	11.81	--
	do	--	--	do	458	10	10H ₂ +100	3000	206-324 (235)	260-324 (235)	206-266 (235)	e-Fe ₂ C, α-Fe	--	--	--
	do	--	--	do	458	10	10H ₂ +100	3000	498-502 (501)	498-502 (501)	470-474 (472)	e-Fe ₂ C, α-Fe	--	--	--
	do	--	--	do	458	10	10H ₂ +100	3000	165-233 (206)	150-217 (178)	173-240 (206)	x-Fe ₂ C	17.31	11.81	--
	do	--	--	do	458	10	10H ₂ +100	3000	233-338 (318)	217-302 (292)	240-352 (338)	e-Fe ₂ C, α-Fe	--	--	--
	do	--	--	do	458	10	10H ₂ +100	3000	230-272 (242)	230-242 (235)	225-250 (241)	e-Fe ₂ C, α-Fe	--	--	--

a/ First figure is temperature at which reaction started, second figure is maximum temperature, third figure is the average temperature of carburizing.

b/ This is a rerun of an earlier preparation that had been oxidized during discharging.

The reaction was followed with an infrared carbon monoxide analyzer (see fig. 2). As the reaction proceeded the rate of disappearance of carbon monoxide could be followed on the analyzer. Upon completion of the reaction the catalyst was quickly cooled under the carbiding gas flow. On reaching room temperature the catalyst was transferred from the Vycor carbiding vessel under a strong flow of carbon dioxide into a collection flask (see figure 5). The collection flask was then placed in a nitrogen-filled dry box. Samples were taken and examined by x-ray diffraction and chemically analyzed. In using a reduced magnetite in place of the leached Raney iron, CO was substituted for the $10\text{H}_2 + 1\text{CO}$ gas and the gas effluent was monitored by the thermal conductivity CO analyzer.

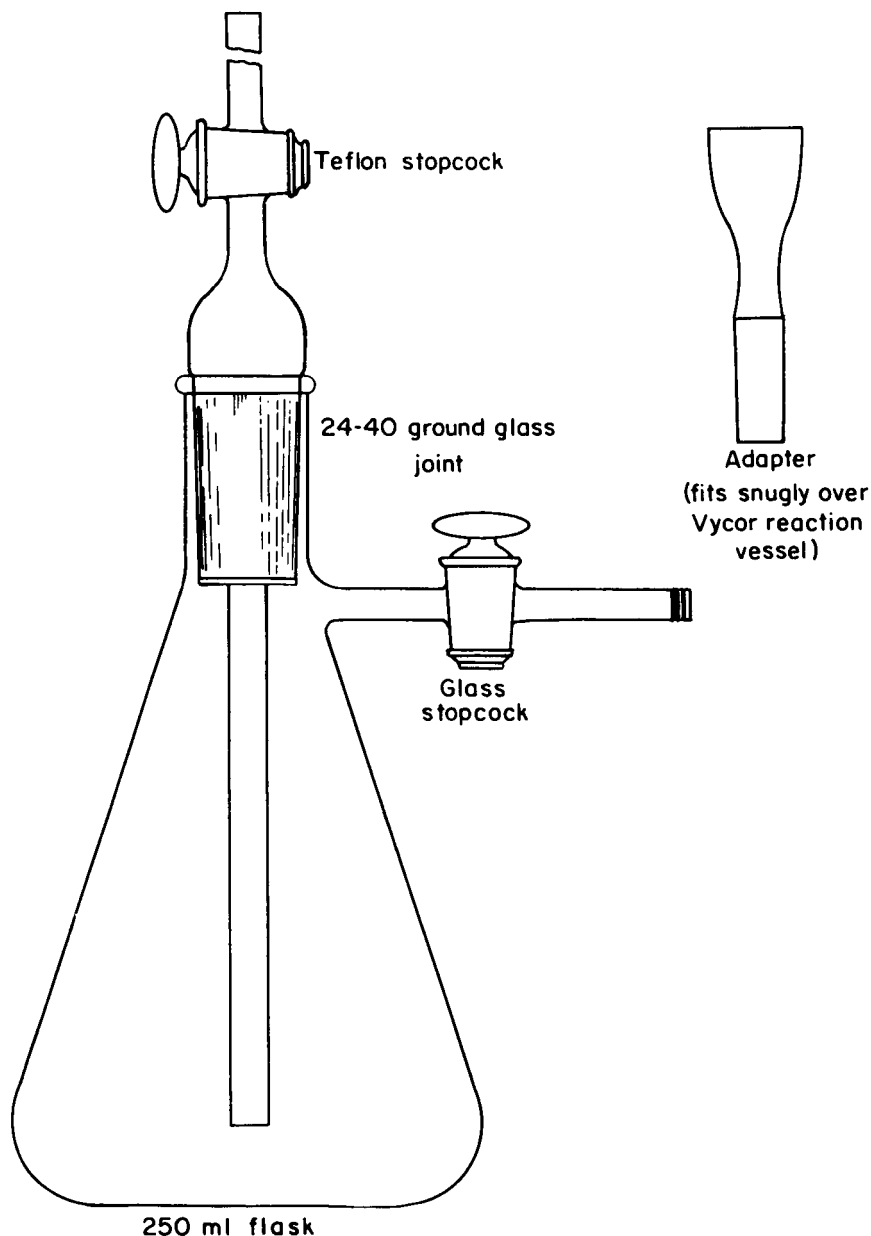


FIGURE 5. - Collection Flask and Adapter Element.

Run 2C showed both ϵ -Fe₂C and Fe₃O₄, and the absence of χ -Fe₂C and α -Fe. This contradicts Johnston and coworkers (8) who stated that the presence of Fe₃O₄ seems to induce formation of χ -Fe₂C in preference to ϵ -Fe₂C. The requirement that iron catalysts contain copper (11) or promoted by a mixture of K₂O and Al₂O₃ (12) for the formation of the hexagonal carbide is not necessary.

The presence of Fe₃O₄ as a minor phase contaminating carbides produced from leached Raney iron was shown to have come from the Raney iron. By reducing the leached Raney iron with hydrogen at 450°C the Fe₃O₄ was eliminated. This is evident in carbide preparation 5C and beyond. Theta iron carbide was produced by first preparing χ -Fe₂C and then converted to θ -Fe₃C by heating at 500°C by the method of Hofer and Cohn (13).

5. Nitride preparations

Procedure

The same unit was used for both reduction and nitriding. The reduced magnetite or leached Raney iron was exposed to a flow of ammonia at the operating conditions indicated in table 5. At the end of the ammonia treatment the catalyst was cooled quickly under the NH₃ flow and then transferred to the receiving bottle under a flow of nitrogen.

Results

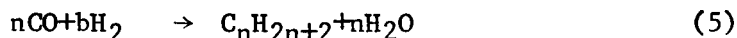
In runs 1N and 2N both ϵ -Fe₃N and γ' -Fe₄N were obtained; ϵ -Fe₃N was the major phase in 1N and γ' -Fe₄N the major phase in 2N. There was complete absence of α -Fe and Fe₃O₄ in both cases. A pure γ' -Fe₄N was prepared from the reduced magnetite in run 7N and from Raney iron in 8N. A pure ϵ -Fe₃N was obtained in 10N. A ζ -Fe₂N was obtained from the magnetite but a mixture with the epsilon as a minor phase was obtained from the Raney iron. The nitrogen content of the γ was 5.04% and the ϵ preparations were individually 7.94, 9.12, 9.61, and 9.75 percent. According to Hofer (7) the nitrogen content of the γ' -Fe₄N ranges from 5.75-5.95%, and the ϵ -Fe₃N from 7.2-11.0%. With the coprecipitated iron-silver mixtures the ϵ -Fe₃N phase was formed with no nitriding occurring with the silver. Silver nitrides have not been reported in the literature. Silver-nitrogen compounds are generally explosive.

b. Results

During the carbiding runs samples of the exit gas were taken and analyzed chromatographically. At 6 hours of carbiding in run No. 3C with $10\text{H}_2+1\text{CO}$ gas, the exit gas composition, on a dry basis, was as follows:

H_2	-----	89.2
N_2	-----	0.2
CO	-----	1.7
CH_4	-----	6.0
C_2H_6	-----	0.8
CO_2	-----	1.6
C_3H_8	-----	0.5

Several reactions are occurring simultaneously:



Equation (1) is the desired reaction. The other concurrent reactions are catalyzed by the iron and iron carbide present.

TABLE 5.- Nitride preparations

Run no	Iron source	Hourly space velocity of NH ₃ , hr ⁻¹	Average bed temp, °C	Duration of nitriding, hrs	Discharge wt, g	Phases by x-ray diffraction	Chemical analyses, wt-%	
							Total Fe	Total N
1N	Magnetite	750	356	6	49.1	ε-Fe ₃ N, γ'-Fe ₄ N	89.90	5.92
2N	do	750	366	6	51.3	γ'-Fe ₄ N, ε-Fe ₃ N	83.20	5.47
4N	do	1000	339	7	48.9	ε-Fe ₃ N, γ'-Fe ₄ N	81.90	7.61
5N	do	1000	340	7	52.3	ε-Fe ₃ N, γ'-Fe ₄ N	82.80	6.57
6N	do	1000	338	12	51.5	ε-Fe ₃ N, ζ-Fe ₂ N	82.4	6.35
7N	do	1000	381	6	50.2	γ'-Fe ₄ N	83.53	5.04
8N	Raney iron	1000	347	7½	46.5	γ'-Fe ₄ N		
9N	Magnetite	1000	342	24	46.6	ζ-Fe ₂ N		
10N	do	1000	345	24	55.5	ε-Fe ₃ N	80.28	7.94
11N	Coprecipitated 3Fe/1Ag	1000	350	25	50.5	ε-Fe ₃ N, Ag		4.85
13N	Raney iron	1000	350	12	46.1	ε-Fe ₃ N	86.47	9.75
14N	do	1000	347	24	44.6	ε-Fe ₃ N		9.61
15N	Coprecipitated 1Fe/1Ag	1000	352	24	58.1	ε-Fe ₃ N, Ag		4.35
16N	do	1000	349	24	57.7	Ag, ε-Fe ₃ N		2.81
17N	Raney iron	1000	352	12	49.1	ε-Fe ₃ N		9.12
18N	do	1000	294	24	99.1	ζ-Fe ₂ N, ε-Fe ₃ N		

6. Nitrocarbide preparations

Procedure

A known weight of iron carbide was transferred to the Vycor reactor tube under a strong flow of CO_2 . After transfer, N_2 was used to flush the CO_2 . A flow of NH_3 was then started and the temperature raised to the desired level and maintained for the duration of the nitriding. When the reaction was completed and on reaching room temperature the catalyst was transferred from the Vycor nitriding vessel under a strong flow of N_2 into a collection flask. The collection flask was then placed in a nitrogen-filled dry box and samples taken for x-ray diffraction and chemical analysis. Conditions for nitrocarbiding are shown in table 6.

Results

Action of ammonia on $\chi\text{-Fe}_2\text{C}$ proceeds as follows: Nitrogen may substitute for carbon in the carbide lattice producing a chi iron nitrocarbide. When sufficient nitrogen to induce instability in the chi iron carbide lattice occurs, the crystal structure will change to the epsilon iron nitrocarbide. In run 1NC complete transformation of the chi to the epsilon occurred. In run 2NC partial transformation occurred. A similar reaction occurs on nitriding theta iron carbide. In 3NC complete transformation to the epsilon phase resulted. This test will be repeated under milder nitriding conditions (300°C for 7 hours) to retain the theta phase.

7. Carbonitride preparations

Procedure

A known weight of iron nitride was transferred to the Vycor reaction tube under a strong flow of N_2 . To avoid stripping the nitrogen in the nitride pure CO was substituted for the $10\text{H}_2+1\text{CO}$ mixture. The CO, flowing through an activated carbon trap, was passed through the nitride at an hourly space velocity of 100. The temperature was set to the desired level on the temperature controller and the gas effluent monitored by the infrared or thermal conductivity unit. Upon completion of the reaction the reactor was quickly cooled under a CO flow. When room temperature was reached the catalyst was transferred from the Vycor carbiding vessel to the collection flask. The collection flask was placed in the inert box, samples were taken for x-ray and chemical analysis. Conditions for carbonitriding are shown in table 7.

TABLE 6.- Nitriding of iron carbides

Run no	Charge	Charge wt, g	X-ray analysis	Gas	Hourly space velocity, hr ⁻¹	Average bed temp, °C	Duration of nitriding, hrs	Discharge wt, g	X-ray analysis	Chemical analysis, wt-%		
										Total C	Free C	Nitrogen
1NC	3C	50.41	X-Fe ₂ C, Fe ₃ O ₄	NH ₃	1000	345	28	-	ε-Fe ₂ X(C,N), Fe ₃ O ₄	-	-	-
2NC	9C	107.85	X-Fe ₂ C	NH ₃	1000	349	24	109.18	χ-Fe ₂ X(C,N), ε-Fe ₂ X(C,N)	11.76	5.93	2.26
3NC	8C	101.58	θ-Fe ₃ C, ε-Fe ₂ C	NH ₃	1000	352	24	104.40	ε-Fe ₂ X(C,N)	-	-	-

TABLE 7.- Carbiding of iron nitrides

Run no	Charge	Charge wt, g	X-ray analysis	Gas	Hourly space velocity, hr ⁻¹	Bed temp, °C	Duration of carbiding, hrs	Discharge wt, g	X-ray analysis	Chemical analysis, wt-%		
										Total C	Free C	Nitrogen
1CN	4N	46.05	ε-Fe ₃ N, γ'-Fe ₄ N	CO	100	309-346 (335) 302-352 (347) 292-315 (307)	11	46.67	ε-Fe ₂ X(C,N)	-	-	-
2CN	7N	43.14	γ'-Fe ₄ N	CO	100	210-295 (273) 295-343 (319)	4 9	43.32	ε-Fe ₂ X(C,N)	-	-	-
3CN	14N	42.51	ε-Fe ₃ N	CO	100	180-350 (249) 350	4 7	43.43	ε-Fe ₂ X	-	-	-

a/ First figure is temperature at which reaction started, second figure is maximum temperature of carbiding, third figure is the average temperature of carbiding.

Results

At temperatures of 350°C, the epsilon and gamma iron nitrides take up carbon to form the epsilon carbonitride. Operating at temperatures of 400° the epsilon phase would probably transform to the chi carbonitride.

Work Plan

Synthesis of 50-100 gram samples of interstitial compounds (see list below) will be made. The samples will be shipped in 15 to 25-gram lots under an inert atmosphere in plastic vials to laboratories designed by NASA. Along with the samples will be information on method of preparation, chemical analysis, qualitative x-ray diffraction analysis, and B.E.T. surface area measurements.

Interstitial compounds of interest:

- 1) Hexagonal-iron carbide
- 2) Hägg-iron carbide
- 3) Cementite
- 4) Gamma-iron nitride
- 5) Epsilon-iron nitride
- 6) Zeta-iron nitride
- 7) Gamma-iron carbonitride; gamma-iron nitrocarbide
- 8) Epsilon-iron carbonitride; epsilon-iron nitrocarbide
- 9) Zeta-iron carbonitride; zeta-iron nitrocarbide
- 10) Iron boride
- 11) Nickel carbide
- 12) Nickel nitride
- 13) Nickel carbonitride
- 14) Cobalt carbide
- 15) Cobalt nitride
- 16) Cobalt carbonitride
- 17) Cobalt boride
- 18) Raney silver-iron alloys and silver-iron oxide
25Ag:75Fe; 50Ag:50Fe; 75Ag:25 Fe
- 19) Silver and iron carbide
- 20) Silver and iron nitride
- 21) Silver and iron carbonitride
- 22) Iron-nickel Raney alloys (same compositions as silver-iron alloys)
- 23) Iron-nickel carbide
- 24) Iron-nickel nitride
- 25) Iron-nickel boride
- 26) Iron-nickel carbonitride

- 27) Raney iron-cobalt alloys
- 28) Iron-cobalt carbide
- 29) Iron-cobalt nitride
- 30) Iron-cobalt boride
- 31) Iron-cobalt carbonitride
- 32) Raney cobalt-nickel alloys
- 33) Cobalt-nickel carbide
- 34) Cobalt-nickel nitride
- 35) Cobalt-nickel carbonitride
- 36) Cobalt-nickel boride
- 37) Raney iron-cobalt-nickel alloys
- 38) Iron-cobalt-nickel carbide
- 39) Iron-cobalt-nickel nitride
- 40) Iron-cobalt-nickel carbonitride
- 41) Iron-cobalt-nickel boride
- 42) Raney iron-cobalt-silver alloys
- 43) Iron-cobalt-silver carbide
- 44) Iron-cobalt-silver nitride
- 45) Iron-cobalt-silver carbonitride
- 46) Iron-cobalt-silver boride
- 47) Raney cobalt-silver alloys and cobalt-silver oxide
- 48) Cobalt-silver carbide
- 49) Cobalt-silver nitride
- 50) Cobalt-silver carbonitride
- 51) Cobalt-silver boride
- 52) Raney nickel-silver alloys
- 53) Nickel-silver carbide
- 54) Nickel-silver nitride
- 55) Nickel-silver carbonitride
- 56) Nickel-silver boride
- 57) Raney iron-silver-gold alloys
- 58) Iron-silver-gold carbide
- 59) Iron-silver-gold nitride
- 60) Iron-silver-gold carbonitride
- 61) Iron-silver-gold boride
- 62) Raney cobalt-silver-gold alloys
- 63) Cobalt-silver-gold carbide
- 64) Cobalt-silver-gold nitride
- 65) Cobalt-silver-gold carbonitride
- 66) Cobalt-silver-gold boride
- 67) Raney nickel-silver-gold alloys
- 68) Nickel-silver-gold carbide
- 69) Nickel-silver-gold nitride
- 70) Nickel-silver-gold carbonitride
- 71) Nickel-silver-gold boride

- 72) Raney nickel-cobalt-silver alloys
- 73) Nickel-cobalt-silver carbide
- 74) Nickel-cobalt-silver nitride
- 75) Nickel-cobalt-silver carbonitride
- 76) Raney nickel-cobalt-gold alloys
- 77) Nickel-cobalt-gold carbide
- 78) Nickel-cobalt-gold nitride
- 79) Nickel-cobalt-gold carbonitride

APPENDIX I

At this point it would be informative to briefly discuss the five general methods of preparing carbides of iron, nickel, and cobalt by gas-phase reactions:

1. Carburization of reduced metal oxides with CO or CO-containing gases.
 2. Carburization of metal oxides with CO or CO-containing gases.
 3. Carburization of reduced metals using hydrocarbon vapors.
 4. Carburization of nitrides of metals using CO or CO-containing gases.
 5. Carburization of leached Raney iron by CO-containing gases.
1. Carburization of reduced metal oxides with CO or CO-containing gases

This was the procedure by which the Bureau prepared most of its carbides. The iron oxide was an alkali-promoted magnetite used in the commercial synthesis of ammonia. The magnetite was reduced with hydrogen at an hourly space velocity of 2,500 at 450°C (14) for a period of 40 hours in a special reaction unit. The amount of reduction was determined by the difference in weight of the magnetite before and after reduction.

The reduced magnetite was returned to the reactor and heated to the desired reaction temperature with a stream of N₂ flowing. CO was then passed over the catalyst at an hourly space velocity of 100. The carburizing was continued for the desired time and the product cooled quickly with a flow of nitrogen.

Basically the problems involve the deposition of carbon, the oxidation of the product when the percentage of CO₂ in the exit gas exceeds 20 percent, and the extremely long time to prepare the pure carbides.

2. Carburization of metal oxides with CO or CO-containing gases

To form carbides from oxides by the reaction $2\text{Fe}_3\text{O}_4 + 14\text{CO} \rightarrow 3\text{Fe}_2\text{C} + 11\text{CO}_2$ require temperatures generally $50^\circ\text{--}100^\circ\text{C}$ higher than that required with the reduced oxides. This method is also unsatisfactory since pure or nearly pure carbides have yet to be prepared by this technique. The probable contamination of the oxide would also be undesirable. Finally, this method has been plagued by large amounts of deposited carbon formed during the reaction.

3. Carburization of reduced metals using hydrocarbon vapors

Thermodynamic data show that it is possible to form any of the carbides of iron at temperatures above 100°C using any of the paraffinic, olefinic, or acetylenic hydrocarbons except CH_4 and C_2H_6 as carburizing gases. The reaction becomes possible at about 200°C with C_2H_6 and about 400°C with CH_4 .

The principle advantage of this method would be that the carbides are formed entirely under reducing conditions, leaving little chance for oxide formation. It has been reported by Podgurski and coworkers (12) that formation of mixtures of $\chi\text{-Fe}_2\text{C}$ and $\alpha\text{-Fe}$ have been made by using propane, butane, and pentane as carburizing gases. However, they indicate that the carburizing was incomplete and that neither Fe_2C nor Fe_3C can be produced as completely as is possible with other methods.

4. Carburization of nitrides of metals using CO or CO-containing gases

Carbon monoxide reacts with nitrides of iron in three ways: (15) First, the carbidic carbon may replace nitrogen with carbon; the crystal structure of the original nitride is maintained. Second, the carbidic carbon may be added to the interstitial nitrogen in the nitride crystals without modifying the crystal structure. Third, the substitution reaction may proceed so far and the carbon-nitrogen ratio may become so large that the carbonitride phase becomes unstable and a phase change reaction takes place. It is possible then to form the carbides of iron from the nitrides of iron. Experimentally the Bureau has found that it is very difficult to remove all of the interstitial nitrogen.

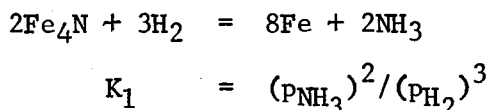
5. Carburization of leached Raney iron by CO-containing gases

Johnston, Heikes and Petrolo (8) have prepared fine powder hexagonal Fe_2C by carburizing 2-4 gram samples of leached FeAl_2 at 240° with a stream of CO and H_2 in which the ratio CO/H_2 varied from 1/3 to 6/1 for a period of 6 hours. It was found that the CO/H_2 ratio was not critical between the limits they investigated. It appeared to the authors that the predominant effect in the stabilization of the hexagonal carbide is the absence of Fe_3O_4 .

We have decided to use this method for several reasons. First, the authors could prepare the ϵ -Fe₂C in a pure form free of χ -Fe₂C. Secondly, the idea of using Raney alloys as the reactant is intriguing due to the high surface area and porosity of the leached alloy. It is known that as the surface area of the reduced iron increases the rate of carbiding increases. The finished carbide should then have a greater surface area since it can be prepared at lower temperatures due to the higher reactivity of the reactant.

Nitrides of Iron

The first detailed work done on iron nitrides was by Emmett and co-workers (16,17). They followed up Noyes and Smith's (18) theory of preparing the nitrides by passing dry ammonia over metallic iron at temperatures around 450°C. Emmett and coworkers determined the equilibrium constants for the reaction



as well as the dissociation pressures of Fe₄N.

It was not until 1951 that the phase diagram for the iron-nitrogen system was completed and published by Jack (19).

The Bureau started work on nitrides of iron at the same time as they were working on the iron carbides. They prepared the nitrides by taking reduced alkali-promoted magnetite and passing anhydrous ammonia over it at temperatures ranging from 350°-450°C depending upon which nitride they were trying to prepare (20,21). In addition to this approach we will also attempt to prepare the nitrides of iron using leached Raney iron as our reactant.

Carbonitrides

In general carbonitrides can be prepared by two methods. The nitrides of the metal can be treated with pure CO or CO-containing gases. The procedure is basically the same as for carbiding the pure metals (15,21). It was found that synthesis gas treatment formed carbon-rich carbonitrides at lower temperatures in shorter times than is possible with CO. X-ray diffraction studies show no distinction between the nitrides and carbonitrides of iron.

The carbides of the metal can be treated with ammonia to produce carbonitrides in the same way as the nitrides of the pure metals can be prepared.

We will attempt to prepare the carbonitrides by both methods as it is not known whether there will be a difference in activity as the oxygen electrode in the H₂-O₂ fuel cell.

Metallic Borides of Fe, Ni, Co

Metallic borides were first prepared metallurgically in the late 19th and early 20th century. For example, iron borides were first prepared by Moissan (22) in 1894. Binet du Jassoneix (23) did further work on the iron borides based on Moissan's original studies.

It was not until 1950 that other than metallurgical methods were developed to prepare the borides of these metals. The probable delay in development lies in the lack of great interest in boron chemistry. For it had not been until the last two decades that major developments and insights have been made in boron related compounds. Paul, Buisson, and Joseph (24) prepared the borides of iron, cobalt, and nickel by the precipitation reaction of sodium borohydride on the salts of these metals in an aqueous solution. This work was said by the authors to be an outgrowth of Schlesinger's studies on the chemical behavior of alkali borohydrides on metallic salts (25). Further studies using this method were done by Kurito, and coworkers (26) in Japan, by Schuele and Dietseret (27), by Rundquist (28) in Sweden, and by the Bureau of Mines (29).

Concerning gas-phase preparation of borides, the only statement found in the literature was a letter written to the editor of Nature by Buddery and Welch, published March 3, 1951. It was stated that several borides were prepared by the passage of hydrogen and boron tribromide vapor over the heated metals (30). Before commenting upon this preparation, it is interesting to note that the Bureau during the period 1953-1956 had attempted to prepare iron borides by passing various gas mixtures of He and B₂H₆ and by passing trimethyl boron gas over reduced iron with no appreciable success.

Through a private communication (31) Buddery indicated that the method he had used would be of general applicability to our own needs. He also sent us a photocopy of a chapter in this Ph.D. Thesis which described all the experimental work he had carried out on this subject.

Having this background behind us it is our intention to attempt to prepare the needed metallic borides of Ni, Co, and Fe by the precipitation method of Schlesinger's and also by adaptation of Buddery's work. It is hoped that the majority of borides can be prepared by Buddery's method using leached Raney iron, which would be more reactive for previously mentioned reasons.

Alloys

At the outset of this project we had the intention of producing a series of binary transition metal alloys of three compositions--75A -25B, 50A -50B, 25A - 75B, percent--which would be carbided, nitrided, carbo-nitrided, nitrocarbided, and borided. The original literature search was done upon this premise.

Since then we have become increasingly interested in preparing these interstitial compounds by using leached Raney alloys. It is now our intention to prepare first a series of ternary transition metal alloys of the Raney type and then after leaching the aluminum to produce the interstitial compounds by the usual methods.

We are presently engaged in a literature search on ternary Raney alloys of transition metals. We expect our experimental work in this area to start during the next quarter.

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